Virtual Answers to Solid Challenges

Michael Francis

Computational materials science lets researchers design and improve materials with a few clicks of a mouse.

The structures and surface chemistry of commercially important solids (including semiconductors, nonlinear optical materials, and catalysts in the form of metal oxides, glasses, and ceramics) are critical to solving technologically significant problems in the chemical, automobile, electronics, and aerospace industries, among others. The structures and electronic properties of these materials and their behavior at surfaces and interfaces are of particular interest to industry. Computational methods, especially quantum mechanical modeling (the most fundamental chemical simulation method), can provide valuable insight.

Computational or in silico materials science helps to optimize products and process design, solve key research problems, and reduce expenditure of time and resources throughout the R&D process. More-focused experimentation can be achieved using calculations and modeling to provide a fundamental understanding of the chemical reactions involved. Thus, researchers can spot "nonstarters" before experimental resources are wasted, and they can design tailor-made materials and processes for specific applications.

Scientists and engineers work toward these goals by applying and combining validated methods such as molecular mechanics, quantum mechanics, mesoscale modeling, analytical instrument simulation, and statistical correlations.

Tools of the Trade

Software can provide valuable information, such as the thermodynamics and energetics of a process, at a relatively low cost. For example, the time and cost of the development of new catalysts can be significantly reduced. In addition, catalysts can be designed accurately to satisfy constraints such as reaction rates or environmental restrictions.

There is a strong emphasis on quantum mechanical calculations in order to understand reaction mechanisms and the role of the individual reaction components. These techniques are used to study the electronic structure and interactions within a material to understand and predict its properties.

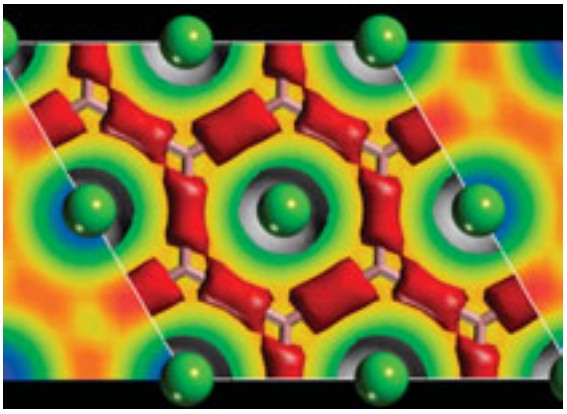

FIGURE 1: Distribution of electron density in a distorted MgB_2 structure, indicating that this particle distortion could act as an electron pump. (Figure courtesy of Accelrys. Used with permission.)

First-principles quantum mechanical software tools, for example CASTEP and DMol^3 (Accelrys, *www.accelrys.com*), are now able to perform electronic structure calculations on models of sufficient size and complexity to represent the chemistry occurring at inorganic surfaces. CASTEP, a tool for modeling periodic systems (systems, including crystals, in which one structural unit repeats many times), is useful for addressing solid-state physics problems including bulk properties and electronic structures. DMol^3, a software tool that can model both periodic and finite (nonrepeating) systems, is useful for simulating chemistry on surfaces and for modeling large systems. Semiempirical and molecular mechanical computational tools enable the study of a large number of systems such as a group of reaction process candidates, or they can simulate single systems with a large number of atoms, to better represent real-world situations. Combining semiempirical and molecular mechanical tools with quantum mechanical tools makes it possible to predict properties and simulate processes accurately and quantitatively.

The Origin of Superconductivity in MgB_2

Quantum mechanical calculations have been used to study and predict properties for many materials of interest to the electronics industry, an important factor in process development, but they have also been used to answer questions at the cutting edge of electronics theory.

For example, Jun Akimitsu's discovery (Aoyama-Gakuin University, Tokyo, *www.bb.aoyama.ac.jp*) of superconductivity in MgB_2 at 39 K has stimulated a great deal of research on the superconducting behavior of this intercalated graphite-like system (*1*) (Figure 1). Superconducting materials are of considerable interest to scientists because at low temperatures they have zero resistivity and undetectable magnetic fields.

Sparked by Akimitsu's discovery, Taner Yildirim of the U.S. National Institute of Standards and Technology's Center for Neutron Research (*www.ncnr.nist.gov*) and colleagues used neutron scattering and computational techniques to unlock the structural secrets behind MgB_2 superconductivity (*2*). They wondered whether the superconductivity arose from the electron–phonon interactions observed in classical superconductors or if there was a more exotic mechanism at work. (A phonon is a quantum unit for measuring acoustic modes of thermal vibration in a crystal lattice.)

The researchers also studied the origin of the high critical temperature (T_c) at

Building a Smarter Tire

Modeling software has been used to supplement and serve the R&D process in, among other industries, the automobile industry. At Continental Tire North America (*www.conti-online.com*), for example, the molecular modeling group has had a profound impact on the success of several high-value projects within the company.

Michael York, a chemist who has been with the company for more than 20 years, explains, "There are ongoing Continental Tire projects which employ molecular modeling to secure a competitive edge in the marketplace. One project involves bonding magnetic material into the sidewall of a tire, which produces a magnetic field for measuring wheel speed, brake torque, and lateral force. Metal does not naturally bond to rubber; therefore, a new type of coupling agent had to be designed. Computational chemistry was used to design a material with high affinity and specificity for the magnetic compound. The results were outstanding."

These techniques drive, refine, and sometimes even replace costly experimentation, saving resources in the process. The researchers used in silico techniques to refine the curing process used in manufacturing tire bladders (or inner tubes), resulting in an increase in the lifetime of the bladders.

York continues, "A refinement in our process was directly initiated based on the knowledge and understanding gained from identifying the adverse reaction by modeling. A saving of over $1.5 million per year was realized."

which the superconducting phase transition occurs in MgB_2. They realized that materials that become superconducting at temperatures closer to ambient would have more practical uses than those that require cryogenic temperatures.

Yildirim and colleagues used the density functional theory (DFT) program CASTEP (*3*) to perform quantum mechanical calculations, then compared the results with experimental neutron-scattering measurements. DFT expresses the total energy of the system as a function (a type of real-valued mathematical function, see *http://mathworld.wolfram.com/Functional.html* for more information) of the total electron density (*4*). The researchers concentrated on studying phonon anharmonicity (interactions between sound waves, or phonons, in a solid that affect its heat transfer properties), pressure dependencies of the phonon anharmonicity, and electron–phonon coupling in MgB_2.

The quantum mechanical calculations gave excellent results, enabling the scientists to report first-principles calculations of the electronic band structure and lattice dynamics for the new superconductor MgB_2. In their work, they pointed out that "the excellent agreement between theory and our inelastic neutron scattering measurements of the phonon density of states gives confidence that the calculations provide a sound description of the physical properties of the system." They found that "the giant anharmonicity and nonlinear electron–phonon coupling revealed is key to

explaining the observed high T_c and large boron isotope effect in MgB_2."

Modeling Chemical Vapor Deposition

Adhesion at the interfaces between semiconductors, metals, and metal oxides is essential to the integrity of many electronic components; the electronic and atomic structure of those interfaces is critical to their function. Chemical vapor deposition (CVD), a key technology in the electronics industry, is a process used to produce thin, high-quality films with precise chemical composition and structural uniformity for the manufacture of electronic devices. Small amounts of a compound are deposited from the vapor phase onto a surface to form a layer that is sometimes only a few atoms deep. Quantum mechanical calculations can be used to model the interactions at the surface of the materials.

Optimizing the CVD process conditions (such as pressure, temperature, precursors, and reactor configuration) for better control of the film growth rate, uniformity, and composition can be achieved using reactor scale models. Such models require detailed understanding of the deposition chemistry, which can be achieved experimentally. However, experiments with silicon wafers are expensive and time-consuming. Thus, theoretical modeling offers an attractive alternative to obtain the input parameters for reactor scale models.

The understanding of gas phase chemistry by far exceeds that of the surface reaction mechanisms. Understanding molecular interactions at surfaces is more complicated from the experimental and theoretical perspectives. The topography and catalytic properties of semiconductor surfaces greatly add to the complexity of the problem. A comprehensive theoretical framework describing the surface deposition is yet to be written.

Silicon oxynitride appears in several electronics applications. Oxide–nitride–oxide structures are widely used in dynamic random access memory (DRAM) and electronically erasable programmable read-only memory (EEPROM) devices. The interfacial region in such structures is silicon oxynitride.

Scientists from Motorola (*www.motorola.com*) and Accelrys have used Accelrys's DFT code DMol[3] to study the deposition of NO on a particular silicon crystal surface, the planar Si(100) surface, which is commonly used as a substrate for the fabrication of commercial semiconductor devices (*5*). The researchers hoped to obtain

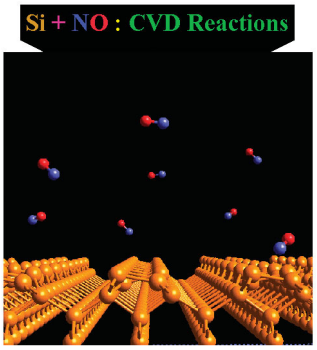

FIGURE 2: NO molecules deposited from the vapor phase onto the (100) surface of a silicon crystal form a silicon oxynitride layer. Incompletely bonded silicon atoms at the surface form covalently bonded pairs, a process called a (2 × 1) surface reconstruction. (Figure courtesy of Accelrys. Used with permission.)

a quantitative and qualitative description of the initial NO deposition on the Si(100) surface and the subsequent growth of the silicon oxynitride film.

To simulate more realistic conditions, the computational model system used a (2 × 1) reconstructed surface, in which pairs of Si atoms in the topmost layer form covalent bonds with each other (Figure 2). Two models of the Si surface were investigated: molecular clusters (the equivalent of modeling a very small portion of a silicon crystal) and "infinite" silicon slabs terminated by hydrogen atoms to minimize the computational effects of not having a truly infinite surface.

Computational tools have enabled scientists to gain new insight into problems.

The simulations revealed the existence of a reaction path with a low-to-nonexistent barrier for breaking the N–O bond. The reaction was found to proceed via elementary steps that include the reduction of bonding between N and O, the breaking of Si–Si bonds, and the formation of Si–N and Si–O bonds.

The study produced a better understanding of the oxynitride film structure, energetics, and physical properties and is a significant move toward being able to fully model the processes involved in CVD.

A Model of a Modern Major Industrial R&D Tool

In a world where companies constantly strive to be one step ahead of the competition, R&D departments aim to improve products to meet customer demands, reduce costs by increasing process efficiency, and be drivers for innovation and growth.

With these goals in mind, researchers and developers need to use all the tools at their disposal to gain and retain a competitive advantage. Computational tools have enabled scientists to gain new insight into key problems through modeling, and these tools are becoming increasingly integral to solving materials science problems in the real world.

Further Reading

Boeri, L.; Bachelet, G. B.; Cappelluti, E.; Pietronero, L. The origin of phonon anharmonicity in MgB_2 and related compounds. *Supercond. Sci. Technol.* **2003,** *16,* 143–146; http://pil.phys.uniroma1.it/superpaperi/SST143.pdf.

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(1) Nagamatsu, J.; Nakagawa, N.; Muranaka, T.; Zenitani, Y.; Akimitsu, J. *Nature* **2001,** *410,* 63–64.

(2) Yildirim, T. The MgB_2 Website at NCNR, U.S. National Institute for Science and Technology, Center for Neutron Research; www.ncnr.nist.gov/staff/taner/mgb2.

(3) CASTEP information page; www.accelrys.com/mstudio/ms_modeling/castep.html.

(4) Density Functional Theory; www.mathub.com/theory/dft.html (free registration required).

(5) $DMOL^3$ information page; www.accelrys.com/mstudio/ms_modeling/dmol3.html.

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